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HIGH TEMPERATURE ANNEALING OF MINORITY CARRIER TRAPS IN IRRADIATED MOCVD n^+p InP SOLAR CELL JUNCTIONS

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Deep level transient spectroscopy has been used to monitor thermal annealing of trapping centers in electron irradiated n^+p InP junctions grown by metalorganic chemical vapor deposition, at temperatures ranging from 500 up to 650K. Special emphasis is given to the behavior of the minority carrier (electron) traps EA (0.24 eV), EC (0.12 eV), and ED (0.31 eV) which have received considerably less attention than the majority carrier (hole) traps H3, H4, and H5, although this work does extend the annealing behavior of the hole traps to higher temperatures than previously reported. It is found that H5 begins to anneal above 500K and is completely removed by 630K. The electron traps begin to anneal above 540K and are reduced to about half intensity by 630K. Although they each have slightly different annealing temperatures, EA, EC, and ED are all removed by 650K. A new hole trap called H3' (0.33 eV) grows as the other traps anneal and is the only trap remaining at 650K. This annealing behavior is much different than that reported for diffused junctions.

INTRODUCTION

Interest in the use of InP as a possible space photovoltaic material was stimulated in the early 1980's when Yamaguchi and co-workers discovered the superior radiation resistance of InP solar cells (refs. 1-3). These cells were made by diffusing S into Zn-doped p-type substrates and had beginning-of-life (BOL) conversion efficiencies near 16% at AM1.5. Both current-voltage (I-V) and deep level transient spectroscopy (DLTS) results were used to show that the presence and annealing of the radiation-induced defects were correlated with solar cell degradation and recovery. In particular, the behavior of the majority carrier DLTS trap H4 appeared to be the cause of both the degradation and recovery (upon annealing) of the solar cell parameters.

Recent research efforts by the present authors using Zn-doped p-InP junctions grown by Spire Corporation using metalorganic chemical vapor deposition (MOCVD) have shown results different from those of Yamaguchi et al. (refs. 4-8). Although the same basic defect structure exists after irradiation, the presence of the radiation-induced defect H4 is seen to correlate only minimally with solar cell recovery following either thermal or injection treatments. It has been suggested recently, however, that it is the presence of another radiation-induced hole trap, H5, which contributes to solar cell recovery in MOCVD material (ref. 9). H5 can be seen following irradiation of more heavily doped cells (~10^{17} cm^{-3}) and grows upon the annealing of H4 in lower doped cells (~10^{16} cm^{-3}). It is possible that other related defects would also contribute to solar cell recovery. It will be shown below that several electron (minority carrier) traps called EA, EC, and ED seem to be related to H5 and therefore might also be important to solar cell behavior.

Many recently published results have considered the introduction and annealing of the majority carrier defects induced by irradiation in p-InP. The effects of minority carrier defects have been largely ignored, until now. This was the motivation for this work because, if minority carrier defects are present, they might be expected to dominate minority carrier diffusion in actual solar cell operation. In p-InP grown by MOCVD, minority carrier defects are formed both following irradiation and annealing and therefore need to be considered in any complete model for the radiation response of InP solar cells (refs. 4,5,7).

McKeever et al. (ref. 4) have shown an interesting correlation between the majority carrier trap H5 and the minority carrier trap EA. DLTS results were presented showing that, as the forward bias across the junction was gradually increased, the intensity of the H5 peak decreased with a corresponding increase in EA. At a forward bias high enough to completely turn the diode on (~0.7V), H5 could not be observed and EA had reached a maximum intensity. This process was completely reversible suggesting that: 1) similar defects are involved, and 2) H5 is an efficient recombination center. It was inferred that, if minority carrier electrons were present, they became trapped at the defect site which then acted as an efficient recombination center for majority carrier holes. Hole emission could not then be observed although electron emission was still possible due to the high concentration present under the forward bias conditions. This observation was important because it suggests that electron traps were also expected to contribute to solar cell degradation and recovery, along with H5.

This paper will present high temperature isochronal thermal annealing results over the range from 500 up to 650K, which is sufficient to completely anneal H5, EA, EC, and ED, leaving behind a new residual defect called H3'.

EXPERIMENT

The devices used in this study were MOCVD n^+p mesa diodes fabricated adjacent to solar cells of the same construction. These solar cells, which were produced by Spire Corporation, have recently yielded efficiencies of greater than 19% at AM0 (ref. 4). The reader can refer to reference 4 for a more complete description of the samples.

DLTS measurements were taken using a Bio-Rad model DL4600 instrument with both liquid nitrogen and helium cryostatic capabilities, enabling measurements to be made over the temperature range 20-500K. Unless otherwise stated, majority carrier measurements were taken using reverse and forward biases of -2 and 0V, respectively, while those for minority carriers were taken using -2 and 1V, respectively. Pulse widths of 50mS were sufficient to ensure a complete filling of the defects.

Thermal annealing up to 500K was performed in situ in the liquid nitrogen cryostat. Above 500K a Lindberg tube furnace was used, in which the samples were annealed in air at atmospheric pressure. The samples were placed in a ceramic tube (alumina) and isochronally heated for 10 minutes while wrapped in aluminum foil. The sample reached the annealing temperature and cooled back to room temperature in times that were negligible compared with the 10 minute anneals. Temperature calibrations were determined using both thermocouple and thermometer measurements. DLTS measurements were performed immediately following each anneal. Capacitance-voltage (C-V) data were also obtained following each successive annealing step in order to monitor the carrier concentration.

1 MeV electron irradiations were performed using a van de Graaff accelerator at NASA Goddard Space Flight Center. The electron fluxes were low enough ($\sim 10^{12}$ $cm^{-2}s^{-1}$) to ensure that no sample heating occurred during irradiations. 10 MeV proton irradiations were performed at the Brookhaven National Labs on Long Island, NY. Dosimetry was accomplished using both Faraday cups and radiachromic films.

RESULTS

Injection Behavior

Particle irradiation of p-InP produces several defects which can be detected using DLTS. Figure 1 shows the typical majority carrier trap DLTS spectrum induced following 1 MeV electron irradiation to a fluence of 10^{16} e^-/cm^{-2}, and then successive thermal annealing treatments up to 500K. Shown are the majority carrier traps H3 and H4, and H5, which have been shown to be associated with displacements in the P- and the In-sublattices, respectively (ref 10). There is little known about actual defect structures in InP. (Although DLTS is a sensitive technique for studying the behavior of deep traps in semiconductor junctions, it does not give information on the actual nature of the defects. This kind of information can only be obtained using such techniques as electron spin resonance and positron annihilation.) The sample used to obtain the data shown in Figure 1 had a pre-irradiation base carrier concentration of $\sim 10^{17}$ cm^{-3}, which causes the peak of majority carrier trap H4 to occur at a temperature below that of majority carrier trap H3 due to junction electric field effects, as reported in reference 8. It can be seen in Fig. 1 that an annealing temperature of 375K substantially reduces the concentration of H4, while only slightly increasing that of H5. This is typical behavior for a junction having a base carrier concentration near 10^{17} cm^{-3}. H3 appears to remain at the same intensity until the sample is heated to 500K, at which it then starts to grow. The activation energy also increases, so the resulting defect appears to be different from H3 and is therefore labelled H3'. The evidence to date indicates that H4, H3, and H3' are closely related defects associated in some way with P vacancies. Figure 2 shows both the majority and minority carrier DLTS spectra obtained following thermal annealing at 500K for 20 minutes. The main traps remaining at this temperature are the minority carrier traps EC, EA, and ED, and majority carrier traps H5. H3, H3', and H2 are also present, although in much smaller concentrations.

Figure 3 shows more detailed information on the injection correlation of H5 with the electron traps than given by McKeever et al. Starting with the spectrum shown in Fig. 2, the forward bias was gradually increased and the DLTS spectrum was measured at several injection levels. The same general correlation is observed as reported by McKeever et al., except that the behavior of three different traps can be closely seen. The reason that McKeever et al. saw only EA is that their samples had been only injection annealed and the residual concentrations of H3 and H4 were large enough to interfere with the DLTS measurements, making EC and ED undetectable. Only when the concentrations of H3 and H4 are sufficiently reduced by thermal annealing, can all three electron traps be seen clearly.

Thermal Annealing

The correlation between H5 and EA, EC, and ED can be further investigated through thermal annealing above 500K. Figure 4 shows high temperature isochronal annealing results from 500 to 650K. The DLTS results show some correlation between the annealing of H5 and EA, EC, and ED, although a one-to-one correspondence is not observed. Not shown in Figure 4 is a DLTS spectrum taken following an annealing temperature of 540K where, although H5 is already annealed to two-thirds of its initial concentration, the electron traps have not yet started to anneal. The electron traps only start to anneal after an annealing temperature of 586K, where H5 is at half the initial intensity. Following the isochronal anneal at 627K, H5 is completely eliminated while EA, EC, and ED are reduced to half intensity. The electron traps are not completely annealed until the temperature is raised to 650K. It should also be noted that majority carrier trap H3' grows during this entire process and becomes the residual defect, not saturating until 650K, when all the other traps have been removed.

DISCUSSION AND CONCLUSIONS

The results presented here have extended the range over which annealing data have been reported for irradiated InP junctions to 650K, at which all the defects except H3' are annealed. The presence of H3' as a residual defect in solar cells made in a way similar to these diodes would probably prevent complete recovery of cell efficiency. It should be noted that an almost complete recovery is observed in diffused junction solar cells where H3' is not formed (see previous paper). Similarly, the inability to anneal H5 in Spire samples at temperatures below 500K has led to Drevinsky's suggestion (ref. 9) that the presence of H5 prevents significant recovery of cells made in this way until the annealing is performed at the high temperatures shown in Figure 4. Drevinsky's results show that there is still substantial radiation-induced carrier removal in the cells even following annealing at 500K. As discussed previously, the defects causing the DLTS peaks H5 and EA, EC, and ED have not yet been identified, although H5 is thought to be associated with displacements in the In sublattice. The high temperature at which these centers anneal suggest, however, that they are not point defects, which are known to anneal in InP at much lower temperatures. Possible candidate defects include complexes of In vacancies or interstitials with impurities.

The different annealing temperatures observed for EA, EC, and ED, and H5, indicate that the correlation between these defects suggested by Figure 3 may be only partial. The disappearance of H5 under injection certainly indicates, however, that it is an efficient recombination center, which supports Drevinsky's conclusion that the presence of H5 reduces solar cell efficiency. It should be noted that H4 is also an efficient recombination center, but the capture of minority carriers leads to rapid injection annealing of H4 in all InP samples even at temperatures far below room temperature. The low temperature at which H4 anneals thermally and the ease with which it is removed by injection shows that H4 is a simple point defect, a conclusion supported by its high introduction rate under 1 MeV electron irradiation.

The different defect annealing behavior observed in the Spire n^+p InP junctions fabricated by MOCVD and the NTT junctions made by diffusion is still unexplained. The different behavior leads to much more efficient recovery at much lower temperatures and injection levels in the photovoltaic parameters of solar cells made by diffusion than by MOCVD. The only obvious difference in the two structures is in the n-type dopant used in the emitter, which is Si in the Spire cells and S in the NTT cells. However, only a fraction of the photocurrent is generated in the emitter region in InP cells under AM0 solar illumination, so it is not immediately apparent why the emitter dopant should have such a profound effect on cell behavior.

It would be interesting to compare the results presented here with the recovery of irradiated Spire solar cells over the same temperature range. It is hoped that this data will be available in the near future.

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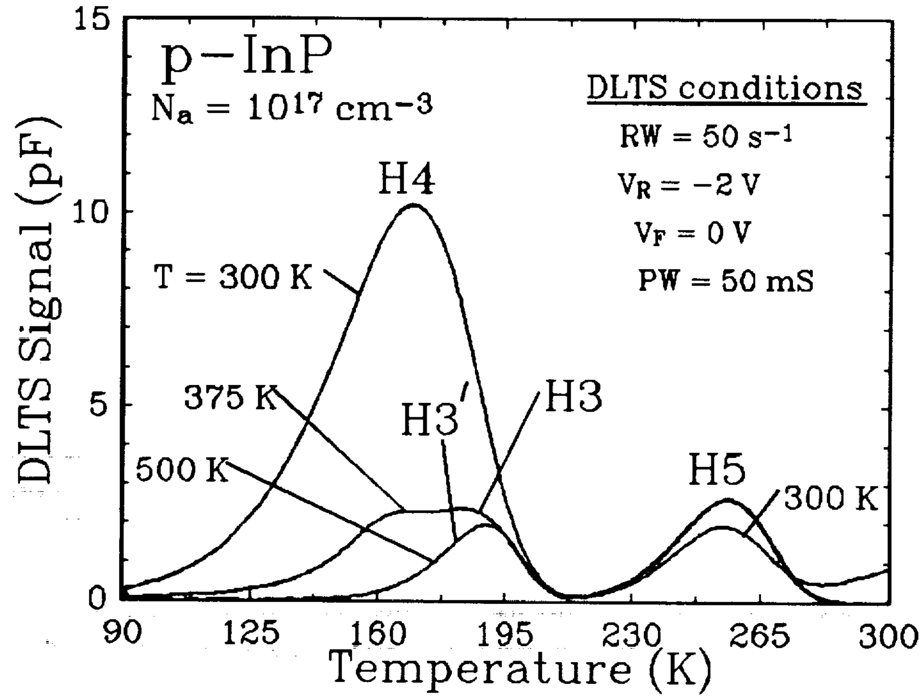

Figure 1 Typical DLTS spectrum of p-InP following 1 MeV electron irradiation and subsequent isochronal thermal annealing steps.

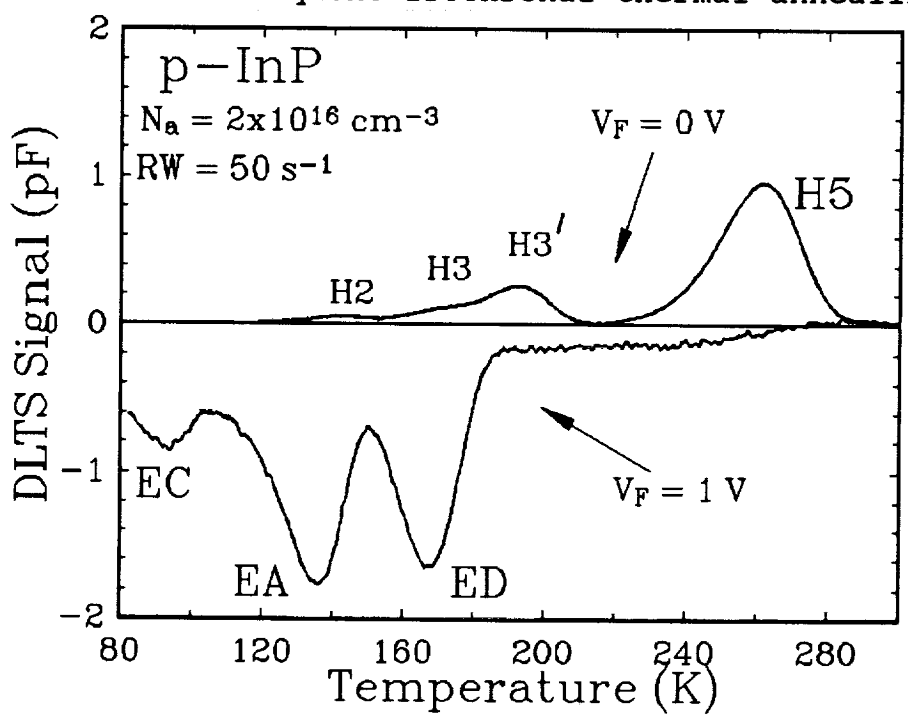

Figure 2 DLTS spectrum showing remaining traps, both majority carrier (hole) and minority carrier (electron), after a thermal anneal at 500K for 20 minutes.

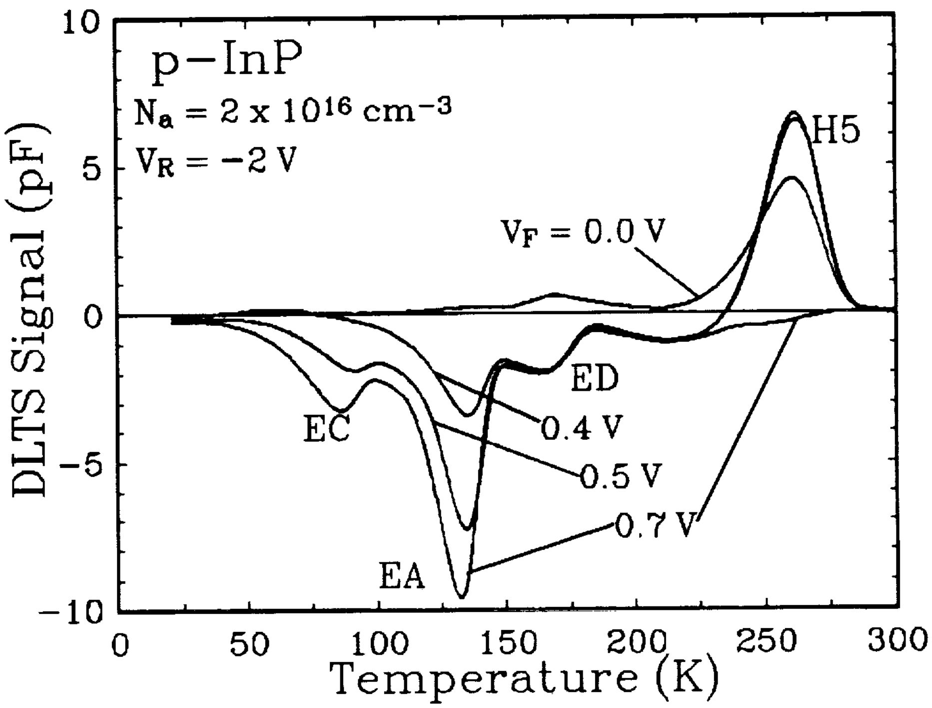

Figure 3 Effect of gradually increasing the forward bias across the junction causing the electron traps to get filled at the expense of H5.

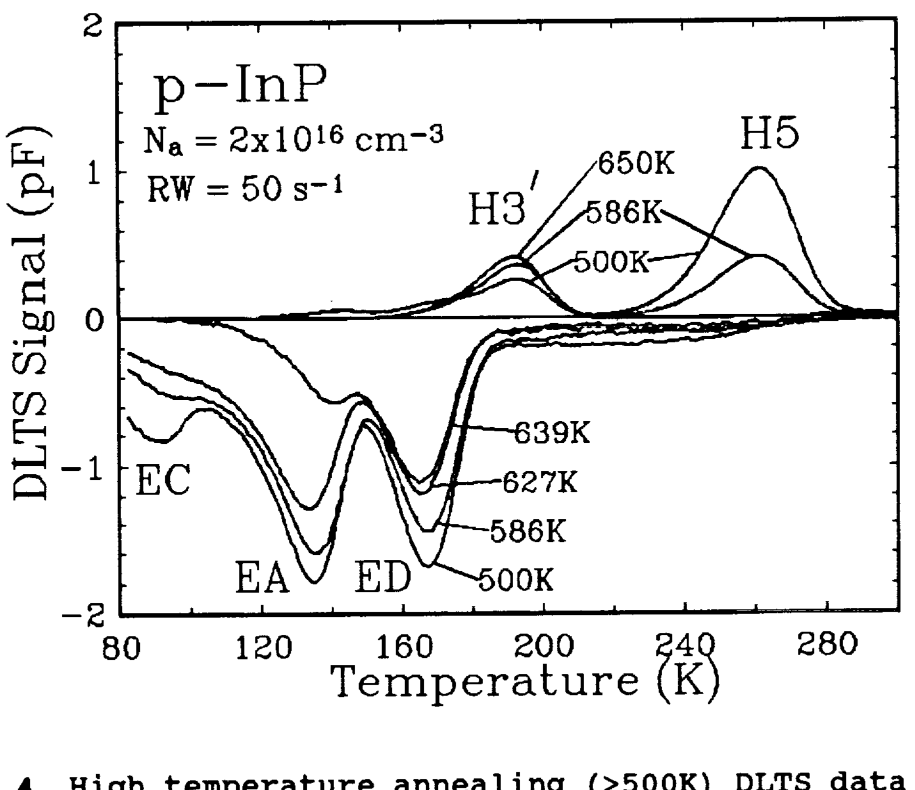

Figure 4 High temperature annealing (>500K) DLTS data showing the eventual anneal of all defects, except for H3', by 650K.